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Ruthenaphosphaalkenyls: Synthesis, structures and their conversion to η^2 -phosphaalkene complexes.

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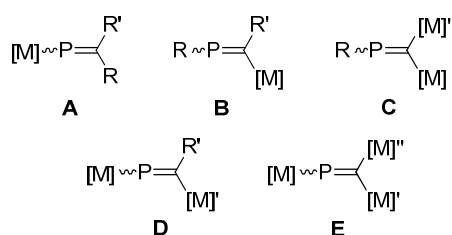
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ABSTRACT: The ruthenaphosphaalkenyls $[\text{Ru}\{\text{P}=\text{CH}(\text{SiMe}_2\text{R})\}\text{Cl}(\text{CO})(\text{PPh}_3)_2]$ ($\text{R} = \text{Me}, \text{Ph}, \text{Tol}$) have been prepared in good yield by the facile hydorruthenation of the respective phosphaalkynes, $\text{RMe}_2\text{SiC}\equiv\text{P}$, with $[\text{RuHCl}(\text{CO})(\text{PPh}_3)_3]$; all three compounds have been structurally characterized in the solid state. Complemented by DFT studies of these, and the precedent $[\text{Ru}\{\text{P}=\text{CH}(\text{tBu})\}\text{Cl}(\text{CO})(\text{PPh}_3)_2]$, the phosphaalkenyl moieties have been established unequivocally to behave as one-electron donors to the coordinately unsaturated, 15-electron $[\text{RuCl}(\text{CO})(\text{PPh}_3)_2]^+$ fragment, corroborating earlier demonstration of nucleophilic character at phosphorus within the *tert*-butyl system. Notwithstanding, the ruthenaphosphaalkenyls are shown to react with the nucleophiles Lipz' ($\text{pz}' = \text{pz}, \text{pz}^*, \text{pz}^{\text{H,CF}_3}, \text{pz}^{\text{Me,CF}_3}$) to afford the η^1, η^2 -chelated pyrazolylphosphaalkene complexes $[\text{Ru}\{\eta^1\text{-N}:\eta^2\text{-P, C-P}(\text{pz}')=\text{CH}(\text{R})\}(\text{CO})(\text{PPh}_3)_2]$, which feature a 3-membered metallacyclic (Ru-C-P) core. The nature of these novel compounds is discussed, alongside preliminary insight into the process by which they are formed.

INTRODUCTION

The chemistry of low-coordinate phosphacarbons has been an active area of research for over four decades,¹ and continues to be a topic of wide-spread interest.² Amidst this constantly developing field, phosphaalkenes ($\text{RP}=\text{CR}'\text{R}''$) have long held particular importance, being among the earliest phosphacarbons to be studied in detail.³ In an organometallic context, while both the η^1 and η^2 -coordination complexes of phosphaalkenes have been studied,⁴ albeit less extensively so for the latter case, a more prevalent interest has surrounded the metallaphosphaalkenes (**A – E**, Chart 1) in which at least one substituent on the 'P=C' moiety is replaced by either a transition metal fragment or main group metal.⁵

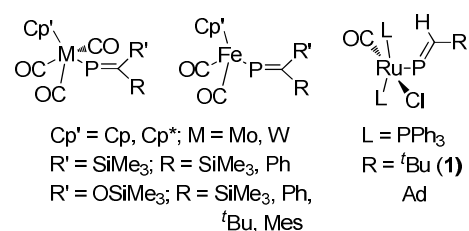
Chart 1: Metallaphosphaalkenyl motifs



With the exception of those of type **E**, all possible metallaphosphaalkene motifs have been realized, albeit that work has been overwhelmingly focused on the *P*-metalla- (type **A**) and *C*-metalla- (type **B**) systems. These constitute intriguing extensions of the phosphacarbon paradigm “the carbon copy” in an organometallic context, particularly in respect of *P*-metallaphosphaalkenyls (type **A**). The first such compound, $[\text{CpFe}(\text{CO})_2\text{P}=\text{C}(\text{SiMe}_3)\text{tBu}]$, described in 1985,⁶ was obtained through an extension of Becker’s methodology, *via* the interaction of $\text{tBuC}(\text{O})\text{Cl}$ with the bis(trimethylsilyl)phosphide complex $[\text{CpFe}(\text{CO})_2\text{P}(\text{SiMe}_3)_2]$.⁷ Subsequently, a range of

such compounds was similarly obtained (Chart 2).⁸ Other prevalent synthetic routes have included: (i) metathesis of *P*-halogenophosphaalkenes with carbonylmetallates;⁹ (ii) metathesis of *P*-silylphosphaalkenes with transition metal halides (L_nMX)¹⁰ and (iii) oxidative addition of *P*-functionalized (Cp^* , Cl) phosphaalkenes to low-valent metal fragments ($\text{M}(\text{NCMe})_3(\text{CO})_3$ $\text{M} = \text{Cr}, \text{Mo}, \text{W}$; “ $\text{Fe}(\text{CO})_5$ ”; $\text{Ni}(\text{PR}_3)_2(\text{cod})$; $\text{Pt}(\text{PPh}_3)_2(\text{C}_2\text{H}_4)$).¹¹ The reduction of phosphaalkynes within the coordination sphere of a transition metal has also found some utility to this end, albeit typically accompanied by oligomerization of phosphaalkyne units.¹² Notably, however, in 1996 Hill and Jones described the facile, stoichiometric, reduction of $\text{tBuC}\equiv\text{P}$ by the ruthenium hydride complex $[\text{RuHCl}(\text{CO})(\text{PPh}_3)_3]$.¹³ Akin to the established alkyne hydorruthenation protocols,¹⁴ this afforded the ruthenaphosphaalkenyl $[\text{Ru}(\text{P}=\text{CHtBu})\text{Cl}(\text{CO})(\text{PPh}_3)_2]$ (**1**),^{13,15} the thiocarbonyl analogue of which was similarly obtained, alongside analogues derived from $\text{AdC}\equiv\text{P}$.¹⁵ Jones subsequently reported the successful double hydorruthenation of his bicyclo-[2.2.2]-octane-1,4-diphosphaalkyne,¹⁶ though Hill’s attempts to prepare an osmium analogue of **1** were thwarted by its facile incorporation of a second equivalent of $\text{tBuC}\equiv\text{P}$ to afford a phosphaalkenyl-phosphaalkene complex.¹⁷

Chart 2: Representative *P*-Metallaphosphaalkenyls



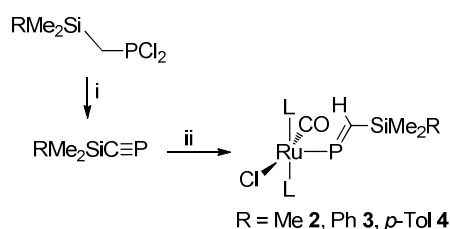
Compound **1** is notable in featuring both a relatively unnumbered phosphalkenyl moiety (*cf.* the classical use of sterically demanding and/or π -donative substituents to confer stability) and apparent unsaturation at the metal center. For early transition metals, such unsaturation results in additional donation of the phosphalkenyl lone pair to the metal, *viz.* adoption of a three-electron phosphavinylidene ligation mode,^{9ac,18} resulting in electrophilicity of the phosphorus center. However, while structural data for **1** have not been described, the demonstration of nucleophilicity at phosphorus,¹⁹ in a series of 1,2 additions across the P–Ru linkage, was deemed characteristic of a ‘bent’ one-electron *P*-phosphavinyl ligand¹⁵ within an overall 16-electron complex; the latter was somewhat supported by isolation of 18-electron complexes upon addition of a series of 2-electron donors (CO, CNR), though a significant trans influence was noted for the phosphalkenyl.^{13,15}

Notwithstanding, while investigating an analogue of **1**, *viz.* [Ru{P=CH(SiMe₃)}Cl(CO)(PPh₃)₂] (**2**), we have noted unexpected ambiphilic behavior. Thus, as we have recently communicated,²⁰ while **2** readily undergoes 1,2 additions consistent with a nucleophilic phosphorus center, its interaction with the pyrazolates [pz’][–] (pz’ = pz, pz*) also results in functionalization at phosphorus. Herein, we describe further investigation of this unusual behavior, including a structural study of the parent phosphalkenyls.

RESULTS AND DISCUSSION

Ruthenaphosphaalkenyl complexes. In a similar manner to that previously described for **1**,¹³ the novel ruthenaphosphaalkenyls [Ru{P=CH(SiMe₂R)}Cl(CO)(PPh₃)₂] (R = Me **2**, Ph **3**, *p*-Tol **4**) were obtained from the reaction of [RuHCl(CO)(PPh₃)₃] with excess of the respective phosphalkyne RMe₂SiC≡P^{21,22} (Scheme 1), the latter generated as toluene solutions by the double dehydrochlorination of RMe₂SiCH₂PCl₂.²³

Scheme 1: Synthesis of phosphalkenyls **2**–**4**.^a



^aReagents and conditions: i) 2 AgOTf, 2 DABCO, toluene; ii) [RuHCl(CO)(PPh₃)₃], CH₂Cl₂

The identities of **2**–**4** follow convincingly from analytical and spectroscopic data. Thus, the ³¹P-NMR spectra exhibit doublet-based resonances associated with the retained PPh₃ ligands (δ_p 34.6, **2**; 33.7 **3**, 33.7 **4**), with mutual coupling (8 Hz) to heavily deshielded resonances (δ_p 548.5, J_{PH} = 21 Hz, **2**; 553.8, J_{PH} = 20 Hz, **3**; 552.6, J_{PH} = 20 Hz **4**) that lie in a region characteristic of *P*-metallaphosphaalkenyls.^{8–12} The latter collapse to triplets in the ³¹P{¹H}-NMR spectra, consistent with loss of the scalar interaction to their respective vinylic proton, the resonances for which are assigned on the basis of ³¹P-¹H HMBC spectra (δ_H 7.28, **2**; 7.40 **3**, 7.41 **4**), alongside their correlation to the carbon (δ_C 168.0 **2**; 163.7 **3**,

165.2 **4**) and silicon (δ_{Si} –9.4 **2**, –14.3 **3**, –14.4 **4**) centers of the phosphalkenyl moiety. Retention of the carbonyl ligand is in each case confirmed by infrared data (ν_{CO} 1920 cm^{–1} **2**; 1938 cm^{–1} **3**, 1936 **4**), the associated ¹³C{¹H}-NMR resonances of which (δ_C 203.0 **2**; 201.9 **3**, 202.54) are also observed.

It is noteworthy that the low-coordinate phosphorus centers of **2**–**4** are significantly more deshielded than that of **1** (δ_p 450.4¹³). We attribute this to the differing substituent at the adjacent alkenic carbon (SiR₃ vs ^{*t*}Bu), given the similar disparity noted between the parent phosphalkynes RC≡P (δ_p : R = Ph –67; SiMe₃ 98.7; SiMe₂Ph 102.7, SiMe₂Tol 103.3). However, one cannot immediately discount the possibility of differing coordination modes; indeed, though compound **1** was concluded to involve a 1-electron phosphalkenyl ligand (*vide supra*),¹⁵ the lack of structural verification, alongside a noted strong trans influence, do not fully preclude the possibility of some phosphavinylidene character (*vide infra*).

From a structural stand-point, the silyl derivatives **2**–**4** (Figures 1–3, Table 1) would seem consistent with the phosphalkenyl being engaged in 1-electron ligation to the metal. Thus, a distinctly ‘bent’ geometry is noted for the phosphalkenyl moiety (\angle Ru–P–C 121.3(2) – 124.4(4) °; \angle P–C–Si 122.5(7) – 125.6(2) °) with no evidence for linearization. The Ru–P linkages are relatively short (d_{RuP} 2.226(2) – 2.2503(10) Å) in comparison to ruthenium-phosphido complexes (2.382 – 2.512 Å²⁴), those of the η^1 -phosphaalkene complexes [Ru{ η^1 -P(E)=CH(R)}Cl₂(CO)(PPh₃)₂] (R = ^{*t*}Bu, E = Au(PPh₃),^{19b} HgFc;^{19c} R = SiMe₃, E = HgPh;²⁰ $d_{(Ru-P)}$ = 2.256(2) – 2.296(2) Å) and that reported for Hill’s 18-electron phosphalkenyl [Ru{P=CH^{*t*}Bu}(O₂CH)(CO)(PPh₃)₂] (2.295(2) Å).¹⁵ They are also shorter than those reported by Peters for [Ru{ κ^4 -Si(C₆H₄PPh₂)₃}{PR₂}] (R = Ph 2.2700(3), ^{*i*}Pr 2.2592(4) Å), which exhibit appreciable Ru=P double bond character, as evidenced by planarity of the Ru–PR₂ unit.²⁵ However, the distances of **2**–**4** do compare well with the Ru←PR₃ distances recorded for other square-based pyramidal ruthenium(II) complexes (2.16 – 2.47 Å²⁴), while the P=C bonds ($d_{P=C}$ 1.655(2) – 1.660(11) Å) are comparable to those of the η^1 -phosphaalkene complexes (1.662(5) – 1.69(2) Å), Hill’s 18-electron system (1.640(8) Å) and phosphalkenyls more generally (1.65 – 1.75 Å).²⁴ It is thus fair to conclude a lack of any higher-order character for the Ru–P linkage; this is also borne out by DFT studies (*vide infra*).

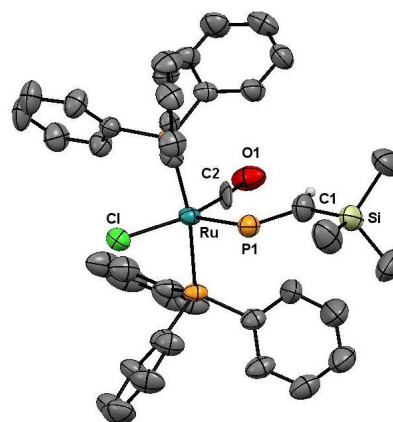


Figure 1: Molecular structure of **2** in molecules of the Et₂O solvate; 50 % thermal ellipsoids, hydrogen atoms omitted for clarity.

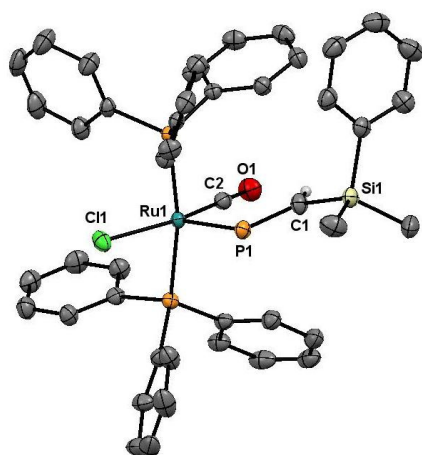


Figure 2: Molecular structure of **3**; 50 % thermal ellipsoids, hydrogen atoms omitted for clarity.

Table 1: Selected geometric data for compounds 2 – 4.^a

	2^b	3	4
Ru–P _{alkenyl}	2.226(2)	2.2468(5)	2.2504(8)
Ru–C _{CO}	1.735(9)	1.835(2)	1.824(3)
P=C	1.660(11)	1.665(2)	1.655(3)
C≡O	1.183(12)	1.143(3)	1.163(4)
Ru–P=C	124.4(4)	121.49(7)	121.31(11)
P=C–Si	122.5(7)	124.88(12)	125.64(17)
P _{PR3} –Ru–P _{PR3}	167.18(7)	166.615(6)	166.84(3)
Cl–Ru–C _{CO}	159.0(3)	162.68(6)	163.57(10)

^aBond distances (Å) and angles (°) with Estimated Standard Uncertainties (esds) in parentheses. ^bThe structure for **2** suffers from some disorder around the carbonyl carbon; associated parameters should be interpreted with caution.

The molecular geometries are otherwise largely unremarkable. The interligand angles about ruthenium (\angle Cl–Ru–CO 162.68(8) – 163.56(12) °; \angle P_{PR3}–Ru–P_{PR3} 166.62(2) – 167.18(7) °) are typical of square-based pyramidal Ru(II), and C≡O distances are similarly consistent. The phosphaaalkenyl moieties are in each case essentially coplanar with the carbonyl ligand (ϕ = 8.2(6) ° **2**, 17.93(10) ° **3**, 17.89(17) ° **4**), with which they also adopt a *cis* conformation, as was observed for [Ru{P=CH^tBu}(O₂CH)(CO)(PPh₃)₂]¹⁵ and has been previously noted for analogous ruthenium vinyl complexes.^{24,26} In the latter cases, this has been attributed to achieving optimal $d_{\pi} \rightarrow \pi^*$ retrodonation to both the carbonyl and alkenyl ligands, coupled with a consequentially significant barrier to rotation about the Ru–C_{alkene} linkage, and a marginal thermodynamic preference for the *cis* rather than *trans* arrangement (ca 2 kcal mol^{–1}) of the two ligands.²⁷ A comparable situation would seem likely for the phosphaaalkenyl analogues.

DFT studies. The ground-state geometries of complexes **1** – **4** were optimized using DFT methods, commencing either from the solid-state data (**2** – **4**) or from hypothetical models (**1** and **2**); in each case comparable geometries were obtained that compare well with the experimental (solid-state) structures of **2** – **4** (see supporting information).

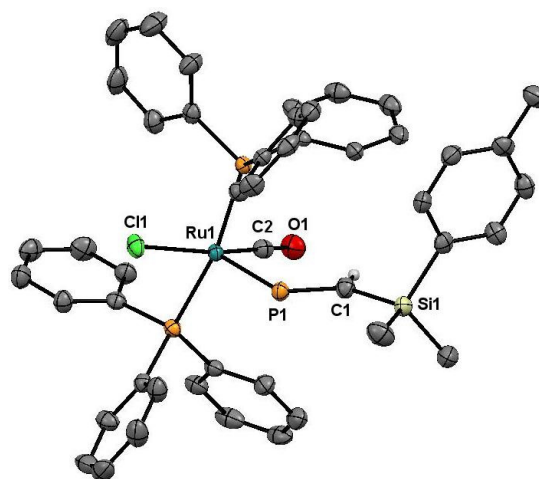


Figure 3: Molecular structure of **4**; 50 % thermal ellipsoids, hydrogen atoms omitted for clarity.

The calculated IR data (ν_{CO}) and ³¹P-NMR isotropic shielding tensors (lanl2dz on Ru; 6-31G** all other atoms) of **1** – **4**, show moderate agreement with experimental data, but do closely reflect the observed trends (Table 2). In particular, the computed ³¹P-NMR shifts for the P_{alkenyl} centers indicate appreciably greater shielding within **1** ($\Delta\delta_{\text{P}} \sim -100$ ppm w.r.t. **2**) compared with the silyl systems; this substantiates the notion that this feature is of purely electronic origin (*i.e.* ^tBu vs SiMe₂R) rather than being the result of any geometric distinctiveness. Indeed, attempts to optimize the geometry of **1** using a phosphavinylidene model resulted in relaxation to the phosphaaalkenyl motif (Figure 4), which exhibits no evidence for involvement of the lone pair in metal binding.

Table 2: Comparative calculated and experimental IR and NMR data.

	$\nu_{\text{CO}} / \text{cm}^{-1}$		$\delta_{\text{P}} (\text{P}_{\text{alkene}})$		
	Calc. ^{a,b,c}	Exp. ^d	B3LYP ^{b,e}	PBEPBE ^{b,e}	Exp. ^f
1	1933.4	1929	482.0	455.4	450.4
2	1938.5	1920	584.4	537.2	548.5
3	1952.2	1938	606.8	558.0	553.8
4	1951.8	1936	604.7	557.9	552.6

^aB3LYP. ^blanl2dz on Ru, 6-31G** on all other atoms. ^cfrequency scaling factor of 0.961 applied. ^dCH₂Cl₂ solutions. ^eUsing GIAO method, referenced against H₃PO₄ at the same level of theory. ^fas CD₂Cl₂ solutions.

For all four complexes the frontier orbitals are dominated by the metal and phosphaaalkenyl fragments. Thus, for **2** – **4** the HOMO involves appreciable bonding overlap between ruthenium and the phosphaaalkenyl σ -framework, and also incorporates the phosphorus lone-pair. A somewhat lesser component of $d_{\pi} \rightarrow \pi^*(\text{CO})$ retrodonation is also apparent. The HOMO-1, which lies essentially orthogonal to the HOMO (with respect to the metal *d* orbitals and alkenyl moiety) and around 0.1 eV lower in energy, is composed of out-of-phase mixing of the metal d_{π} orbital and phosphaaalkenyl π -system, and in the cases of **3** and **4** a small contribution from the arene π -orbitals. For **1**, the HOMO and HOMO-1 are reversed, though again close in energy (0.09 eV) and with the same general composition.

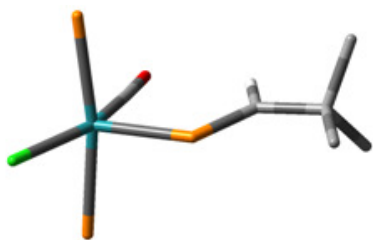


Figure 4: Optimized core geometry of **1**, with phenyl rings and ancillary hydrogen atoms omitted for clarity. Selected bond distance (Å) and angles (°): Ru–P 2.318, P=C 1.680, Ru–CO 1.846, C=O 1.166, Cl–Ru–C 159.02, Ru–P–C 118.05 P=C–C 126.54.

In all cases the LUMO is appreciably separated from the HOMO (3.76 – 3.87 eV), largely metal-based, and accessible to nucleophiles through the basal plane. Interestingly, for **2** – **4** the LUMO+1, which is only modestly higher in energy (ca 0.6 eV), involves an appreciable contribution from the phosphalkenyl π^* orbital; the equivalent orbital of **1** is at LUMO+2, ca 0.8 eV above the LUMO. This is significant, given that NBO calculations indicate an appreciable δ^+ character at the alkenyl phosphorus atom (0.55 – 0.76). Taken together, these features would seem to imply the possibility of at least some electrophilic character for this center, alongside the unequivocally established nucleophilicity associated with the accessible lone pair (HOMO). This has potential implications in respect of the noted ambiphilicity of these systems (*vide infra*).²⁰

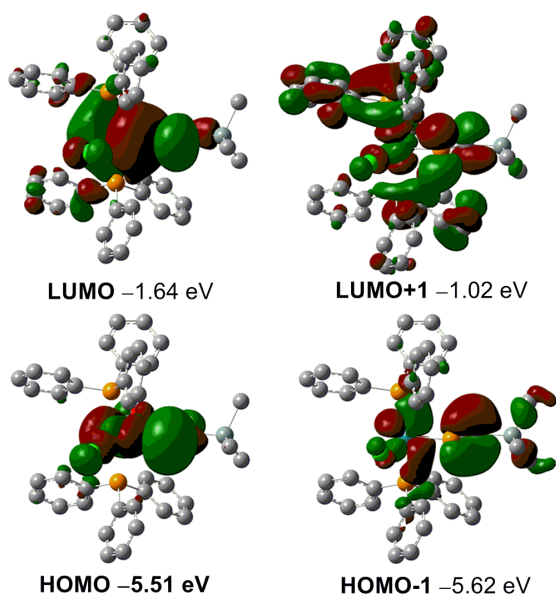
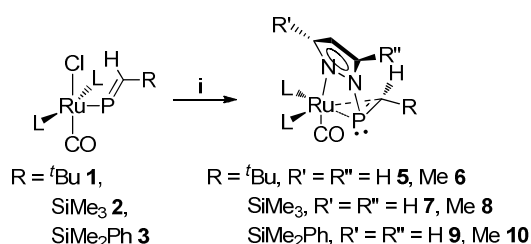


Figure 5: Representative Frontier Orbitals for compound **2**.

Synthesis of η^2 -phosphaalkene complexes. The ruthena-phosphaalkenyls **1** – **3** all react readily, in thf solution, with single equivalences of the lithium pyrazolates Lipz' (pz' = pz, pz*) to afford in each case high yield of a single species (**5** – **10**, Scheme 2). As we have previously communicated,²⁰ the connectivity of compounds **7** and **8** was established from X-ray diffraction data, which were readily reconciled with characteristic features of the multinuclear NMR spectra. Thus, while **5**, **6**, **9** and **10** have yet to yield X-ray quality crystals, their comparable nature is apparent from their spectroscopic

signatures (Table 3). In all cases three (1:1:1) mutually coupling resonances are apparent in the $^{31}\text{P}\{^1\text{H}\}$ -NMR spectra, in a region (10 – 60 ppm) typically characteristic of saturated phosphorus centers, while the heavily deshielded phosphalkenyl resonance has been lost. Notwithstanding, retention of the ^tBu (**5**, **6**) or SiMe_2R (**7** – **10**) moieties is apparent from the ^1H NMR spectra (supported by ^1H - ^{29}Si correlation for **7** – **10**), the respective resonances integrating consistently against those in the aromatic region, which indicate retention of both PPh_3 ligands. Moreover, ^1H and ^{13}C NMR resonances associated with the P–CH unit are observed, identified on the basis of correlation experiments, albeit in significantly more shielded positions; the 'P–CHR' unit can thus be concluded to be in-tact, albeit no longer phosphalkenyl in nature. Finally, retention of the carbonyl ligand is confirmed by both characteristic infrared and $^{13}\text{C}\{^1\text{H}\}$ NMR data.

Scheme 2: Reactions of **1 – **3** with Lipz' (pz' = pz, pz*).**^a



^aReagents and conditions: i) Lipz' (pz' = pz, pz*), thf, r.t., 1 h. Comparable methodology is used to obtain **11** to **14** from Lipz'^{CF3} and Lipz'^{Me,CF3}

The precise nature of the three-membered (Ru–C–P) cyclic core of these compounds is a matter of intrigue. The crystallographic data²⁰ for **7** and **8** indicated significant pyramidalization about the C_{alkene} center ($\angle \text{P–C–H}$ 112.8°, $\angle \text{Si–C–H}$ 112.8°, $\angle \text{P–C–Si}$ 116.7°) with concomitant lengthening of the P–C linkage (1.793(6) Å), superficially consistent with a ruthena-phosphirane geometry. Indeed, ^1H and ^{13}C NMR spectroscopic data would also seem to support such formalism, the 'P–CH' moiety exhibiting shifts consistent with a saturated system (**7**: δ_{H} 1.59, δ_{C} 47.5; **8**: δ_{H} 1.62, δ_{C} 44.9). The C–H coupling magnitudes for the 'P–CH' moiety (J_{CH} 137 Hz **7**, 123 Hz **8**) are, however, more ambiguous, being intermediate between those characteristic of ' sp^3 ' (cf. 125 Hz in CH_4) and ' sp^2 ' (cf. 156 Hz in C_2H_4)²⁸ models; moreover, minimal perturbation of the P–C coupling magnitude ($^1J_{\text{PC}}$ ~79 Hz; cf. $^1J_{\text{PC}}$ = 77 Hz in **3**) is also superficially consistent with retention of appreciable ' sp^2 ' character. Intermediate character is also reflected in the fact the P–C linkage remains shorter than both a typical $\text{P}(\text{sp}^3)\text{--C}(\text{sp}^3)$ single bond (1.855(19) Å)²⁹ and those of other known phosphiranes (1.8 – 1.9 Å²⁴).

The spectroscopic data for all compounds **5** – **10** show a consistent trend, though it is again noted that replacement of silyl with *tert*-butyl results in significant deshielding of the 'P–CH' unit (cf. **1** vs **2** – **4**). This is markedly more pronounced than for the parent phosphaalkenyls, which may suggest a more 'alkene-like' character than for the silyl derivatives; however, the magnitude of $^1J_{\text{CH}}$ in **6** (137 Hz) is comparable, while a slightly greater variation in $^1J_{\text{PC}}$ coupling (67 Hz **5**, 69 Hz **6**) over the alkenyl ($^1J_{\text{PC}}$ ~ 59 Hz **1**¹³) may reflect a marginal increase in *s*-character. Finally, infrared spectroscopic data for **5** – **10** indicate a significant reduction in the

Table 3: Spectroscopic data for η^2 -phosphaalkene complexes **5 – **14**.^a**

	R	R'	R''	δ_P^b		δ_C^c	δ_H^c	$\nu_{CO}^e / \text{cm}^{-1}$	$k_{CO} / \text{N cm}^{-1}$
				P=C	PPh ₃	P=C	P=CH ($^1J_{CH} / \text{Hz}$) ^d		
5	^t Bu	H	H	38.8	44.2, 42.5	81.6	2.84	1906	14.68
6	^t Bu	Me	Me	14.7	45.5, 41.4	79.8	2.90 (137)	1902	14.62
7	SiMe ₃	H	H	58.7	46.6, 42.0	47.6	1.59 (137)	1907	14.69
8	SiMe ₃	Me	Me	32.9	46.6, 39.2	44.9	1.62 (123)	1906	14.68
9	SiMe ₂ Ph	H	H	57.0	47.0, 41.7	45.1	1.72 (135)	1913	14.79
10	SiMe ₂ Ph	Me	Me	32.3	47.0, 38.9	41.8	1.77 (128)	1910	14.74
11	SiMe ₃	H	CF ₃	76.6	47.7, 41.5	47.1	1.78 (136)	1912	14.77
12	SiMe ₃	Me	CF ₃	64.6	46.9, 38.4	45.2	1.76 (129)	1909	14.72
13	SiMe ₂ Ph	H	CF ₃	74.9	48.0, 41.3	46.7	1.91 (136)	1915	14.82
14	SiMe ₂ Ph	Me	CF ₃	62.7	47.2, 38.3	41.8	1.97 (131)	1909	14.72

^aNMR spectra recorded in CD₂Cl₂ for compounds **5** – **10** inclusive; CDCl₃ **11** – **14**. ^breferenced to 85 % H₃PO₄. ^creferenced to SiMe₄. ^dmeasured using coupled ¹H-¹³C- HSQC spectra. ^erecorded as solutions in CH₂Cl₂.

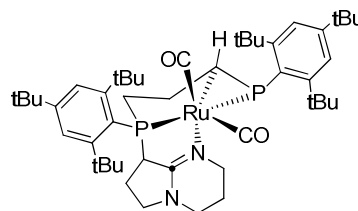
carbonyl stretching frequencies in comparison to the parent phosphaalkenyls. Indeed, while ν_{CO} for the latter are entirely consistent with Ru(II) (*vide supra*; 1929 cm⁻¹ for **1**), those of **5** – **10** are more akin to the limited range of Ru(0) monocarbonyls reported to date (1910 – 1880 cm⁻¹),³⁰ while the force constants for the C=O bond are consistent with those derived from Ru(0) dicarbonyls.³¹

Taken together, these data suggest that compounds **5** – **10** are perhaps best described using the Dewar-Chart-Duncanson model, and formulated as η^2 -phosphaalkene complexes. Thus, $d_\pi \rightarrow \pi^*_{(P=C)}$ retrodonation can be considered a dominant contribution to metal-ligand binding (albeit potentially diminished in complexes **5** and **6**, a corollary of reduced acceptor character of *tert*-butyl compared with silyl), as was described by Cowley for [Ni{ η^2 -(Me₃Si)₂C=PCH(SiMe₃)₂}(PMe₃)] ($d_{P=C}$ 1.773(8) Å),³² which also exhibited a significantly low-frequency resonance for P_{alkene} (δ_P 23). More recently, Ionkin described a similar situation (δ_P 54) for his chelated phosphaalkene complex (Chart 3),³³ the significant shift from the free ligand (δ_P 248), which was mirrored in the ¹³C data (δ_C 67, *cf.* 181 for the free ligand), being deemed consistent with an η^2 -coordination mode. These data fit well with the trends noted herein.

A further notable feature in the spectroscopic data of **5** – **10** is the appreciable shielding of the P_{alkene} center in the 1,3-dimethylpyrazole derivatives, compared with their pyrazole analogues, presumably reflecting the enhanced donor strength of pz* over pz. This was verified by preparing the analogues **11** – **14**, which incorporate pz^{CF₃} and pz^{Me,CF₃} moieties.³⁴ The spectroscopic data (Table 3) in each case reflect the anticipated trend in δ_P for the P_{alkene} center (pz* < pz < pz^{Me,CF₃} < pz^{CF₃}), the more electron-withdrawing CF₃ moiety imparting appreciable deshielding. It is noteworthy that in each of **11** – **14** a single positional isomer is apparently formed in respect of the pyrazolyl substituents, the assignment of which is non-trivial in lieu of structural data. However, while the CF₃ moieties exhibit correlation to both P_{alkene} and one of the PPh₃ ligands, only for the former is an appreciable coupling observed ($^1J_{PF} \sim 20$ Hz), consistent with CF₃ being proximal to the P_{alkene} center. This can be rationalized in terms of the steric demand of accommodating the bulkier CF₃ (*cf.* Me) between flanking PPh₃ units. Indeed, reacting **2** or **3** with Lipz^{(CF₃)₂}, for which

this is unavoidable, fails to afford the fluorinated analogues of **8** and **10**, resulting instead in degradation of the ruthenaphosphaalkenyls; comparable results are noted with Lipz^{(*t*Bu)₂}, thus negating the possibility of an electronic effect associated with the bis-trifluoromethyl system.

Chart 3: A chelated ruthenium η^2 -phosphaalkene complex.



DFT studies. The optimized ground-state geometries of **5** and **7** (Figure 6) both show good agreement with the solid state data for the latter.²⁰ There is only marginal variation in geometry about the P–CH moiety, **5** exhibiting a slightly wider P–C–R angle (119.24 °, *cf.* 117.23 ° in **7**) and increased displacement of carbon from the metal center (2.244 Å, *cf.* 2.240 Å in **7**), while other parameters are comparable. This would seem to exclude significant variation in the extent of ‘alkene’ character being responsible for the observed spectroscopic variations between silyl and ^tBu systems. Indeed, though the calculated isotropic shielding tensors for **5** and **7** (³¹P, ¹³C and ¹H) are in less close agreement than for their parent phosphaalkenyls (*vide supra*), they do mirror the experimental trend. Thus, for the ‘P–CH’ fragment, the phosphorus center of **5** resonates at somewhat lower frequency than that of **7** ($\Delta\delta_P = -13.6$ *cf.* -19.9 expt.), while significant deshielding is also apparent for both ¹³C and ¹H nuclei ($\Delta\delta_C = 31.4$, $\Delta\delta_H = 1.25$; *cf.* 34.0 and 1.22 expt.). The calculated carbonyl stretching frequencies correlate well with the experimental data, the significant decrease from those of the parent phosphaalkenyls being consistent with reduction of the metal (Ru(II) → Ru(0)), as previously inferred (*vide supra*).

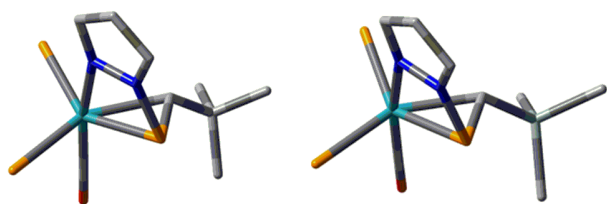


Figure 6: Optimized geometries of **5** (left) and **7** (right), with hydrogen atoms and phenyl rings omitted for clarity.

Table 4: Calculated spectroscopic data for **5** and **7**.

	B3LYP ^{a,b}			PBEPBE ^{a,b}			$\nu_{\text{CO}}^{\text{a,c}}/\text{cm}^{-1}$
	δ_{P}	δ_{C}	δ_{H}	δ_{P}	δ_{C}	δ_{H}	
5	94.1	96.9	3.52	73.3	100.9	3.99	1912.8
7	108.1	65.3	2.30	82.6	65.8	2.1	1915.9

^alan12dz on Ru, 6-31G** on all other atoms. ^bdata for the P–CH fragment, calculated using the GIAO method, referenced against H₃PO₄ and Me₄Si at the same level of theory. ^c B3LYP, frequency scaling factor of 0.961 applied.

Mechanistic considerations. The mechanism by which compounds **5** – **14** form from the respective phosphalkenyls and Lipz' is the subject of on-going experimental and computational studies; however, brief comment is warranted. Intuitively, one might anticipate nucleophilic attack at the ruthenium center, given its predominant contribution to the LUMO and accessibility through the basal plane. Indeed, complex **1** was shown to readily add donors (CO, CNR) at this site,¹⁵ albeit that an apparently strong *trans* influence imparted significant lability. Moreover, the reaction of **1** with the carboxylate salts Na[O₂CR] (R = H, Fc) was shown to afford [Ru{P=CH^tBu}(O₂CH)(CO)(PPh₃)₂] via formal nucleophilic displacement of chloride,¹⁵ presumably via an associative mechanism. It is also reasonable to consider that in the reaction of **1** or **2** with electrophilic species such as RHgCl, MeI or AuCl(L),^{15,19a,b,e,20} the ensuing 1,2 addition across the Ru–P bond involves installation of a nucleophilic fragment (X[−]) at the vacant metal site, though whether this is concomitant with addition of the electrophilic fragment to phosphorus, or facilitated by it, has not been established.

However, one cannot arbitrarily dismiss the possibility of initial nucleophilic attack at the phosphorus center. While nucleophilicity at this site is characteristic of 1-electron phosphalkenyls and has been well established for both **1**¹⁵ and **2**,²⁰ NBO analysis (*vide supra*) has provided evidence of appreciable δ^+ character. Moreover, as noted, the $\pi^*_{(\text{P}=\text{C})}$ orbital is a significant component of the LUMO+1 (LUMO+2 in **1**), which lies moderately close in energy to the LUMO ($\Delta_{\text{E}} \sim 0.6$ eV), thus offering a viable competitive pathway. Notwithstanding, in the formation of **11** – **14**, we have inferred the influence of sterics in directing the bulkier CF₃ substituent (*cf.* H, Me) to orient away from the metal center; we have also noted this in the reaction of **2** with Lipz'^{Bu}.³⁵ While not fully excluding the possibility of attack at phosphorus,³⁶ this outcome would necessarily follow from an associative addition to ruthenium, sterics likely precluding approach of the more encumbered (α -CF₃ or ^tBu) nitrogen center. Thus, while we are yet to reach a definitive conclusion, weight of evidence would currently suggest initial addition to the ruthenium center, presumably followed by elimination of LiCl. However, the pro-

cess by which the putative pyrazolate complexes [Ru{P=CH(R)}(pz')(CO)(PPh₃)₂] subsequently convert to [Ru{ η^1 -N: η^2 -P,C-P(pz')=CH(SiMe₃)}(CO)(PPh₃)₂] with concomitant reduction of the metal remains unclear.

CONCLUDING REMARKS

We have described the synthesis of several ruthenaphosphalkenyl complexes by the hydorruthenation of the silylphosphalkynes RMe₂SiC \equiv P (R = Me, Ph, *p*-Tol), and provided the first structural (X-ray and DFT) characterization of these intriguing compounds. The complexes are thus confirmed to adopt square-pyramidal geometry about ruthenium and comprise a formal 1-electron phosphalkenyl ligand, as was previously inferred for [Ru{P=CH(^tBu)}Cl(CO)(PPh₃)₂] on the basis of reactivity studies. While that latter remains elusive to crystallographic study, DFT has provided adequate evidence to confirm a comparable geometry to its silyl counterparts.

All of the complexes are found to react with lithium pyrazolates, seemingly resulting in reduction of both the metal (Ru(II) \rightarrow Ru(0)) and phosphalkenyl moiety. The resulting complexes exhibit a metallacyclic core (Ru–P–C) that might feasibly be described as a ruthenaphosphirane, the Ru–P bond of which is additionally bridged by the pyrazolyl group. However, spectroscopic and structural data are inconclusive, being equally consistent with the η^2 -coordination of a phosphalkene, tethered by the pyrazolyl moiety, with a dominant bonding contribution from $d_{\pi} \rightarrow \pi^*_{(\text{P}=\text{C})}$ retro-donation. Indeed, on balance, we currently favor this description, based on the Dewar-Chatt-Duncanson model. Regardless of the correct formalism, the process by which these novel complexes are obtained is equally intriguing and remains to be firmly established. While it is not currently possible to fully discount the direct nucleophilic attack at phosphorus – which would imply true ambiphilic character for the phosphalkenyl ligand, for which some support is found – evidence would seem to favor initial addition of the pyrazolate to ruthenium. However, the full mechanistic features of this reaction remain to be established, and are the subject of on-going investigations.

EXPERIMENTAL SECTION

General Methods. All manipulations were performed under strict anaerobic conditions using standard Schlenk line and glovebox (MBraun) techniques, working under an atmosphere of dry argon or dinitrogen respectively. Solvents were distilled from appropriate drying agents and stored over either molecular sieves (4 Å, for DCM and THF) or potassium mirrors. General reagents were obtained from Sigma-Aldrich or Fisher and purified by appropriate methods before use, precious metal salts were obtained from STREM. [RuHCl(CO)(PPh₃)₃],³⁷ ^tBuC \equiv P,³⁸ RMe₂SiCH₂PCl₂ (R = Me, Ph),²³ Me₃SiC \equiv P^{20,39} and [Ru{P=CH(^tBu)}Cl(CO)(PPh₃)₂]^{13,15} were prepared by literature methods. Unless otherwise stated NMR spectra were recorded at 303 K, on Varian VNMRs 400 (¹H 399.50 MHz, ¹³C 100.46 MHz, ¹⁹F 375.87, ³¹P 161.71 MHz, ²⁹Si 79.37 MHz); VNMRs 500 (¹H 499.91 MHz, ¹³C 125.72 MHz) or 600 (¹H 599.69 MHz, ¹³C 150.81 MHz, ³¹P 242.83 MHz) spectrometers were used in selected instances. All spectra are referenced to external Me₄Si, 85 % H₃PO₄ and CCl₃ as appropriate. Carbon-13 spectra were assigned by recourse to the 2D (HSQC, HMBC) spectra; phosphalkenic proton and silicon shifts were determined indirectly by ¹H-³¹P and ¹H-²⁹Si correlation (HMBC). Mass spectrometry was performed by Dr A. Abdul-Sada of

the departmental service. Elemental analyses were obtained by Mr S. Boyer of the London Metropolitan University Elemental Analysis Service.

X-ray diffraction studies. Single crystal X-ray diffraction data were recorded on an Agilent Xcalibur Eos Gemini Ultra diffractometer with CCD plate detector using Mo-K α (λ = 0.71073) or Cu-K α (λ = 1.54184) radiation. Structure solution and refinement were performed using SHELXS⁴⁰ and SHELXL⁴⁰ respectively, running under WinGX⁴¹ or Olex2.⁴²

DFT calculations. Calculations were performed using Gaussian 09W, Revision C.01,⁴³ running on an Intel Core i5-2500 (quad, 3.3 GHz), equipped with 4 GB RAM; results were visualized using GaussView 5.0. Geometries were optimized with the hybrid density functional B3LYP, using the RECP basis set Lanl2dz for Ru and 6-31G** for all other atoms. Minima were characterized by frequency calculations, and calculated frequencies adjusted by standard scaling factors. NMR shielding tensors were calculated at the same level of theory with both the B3LYP and PBEPBE functionals using the GIAO method, and compared against those similarly calculated for the respective reference standards to derive chemical shifts.

(*p*-Tol)Me₂SiCH₂Cl. To a cooled (−10 °C), stirred ethereal solution (30 cm³) of ClMe₂SiCH₂Cl (10 cm³, 0.076 mol) was added a thf solution of *p*-TolMgBr (57 cm³, 1.33M, 0.065 mol). After 45 min. the mixture was brought to reflux for 18 h., then allowed to cool to ambient temperature with continued stirring. The solvents were removed by distillation at ambient pressure, then the residue distilled under reduced pressure (2.3 mbar, 55 °C) to afford (*p*-Tol)Me₂SiCH₂Cl as a colorless liquid (6.6 g, 43 %) which was identified on the basis of literature data.⁴⁴ ¹H NMR (CDCl₃): δ : 0.41 (s, 6H, Si(CH₃)₂), 2.37 (s, 3H, CH₃-Ar), 2.94 (s, 2H, CH₂Cl), 7.21 (d, J = 7.71 Hz, 2H, Ar-H), 7.45 (d, J = 7.71, 2H, Ar-H). ¹³C NMR (CDCl₃): δ 4.3 (s, ¹J_{SiC} = 54.1 Hz, Si(CH₃)₂), 21.6 (s Ar-CH₃), 30.7 (s, CH₂Cl), 128.98 (s, Ar-H), 133.9 (s, Ar-H). ²⁹Si NMR (CDCl₃): δ −4.1.

(*p*-Tol)Me₂SiCH₂PCl₂. Following from literature methods for related compounds,²³ TolMe₂SiCH₂Cl (6.6 g, 0.033 mol) in ether (15 cm³) was added, drop-wise, to a stirring suspension of activated Mg (2.0 g, 0.08 mol) in ether (20 cm³), at a rate to maintain reflux. Stirring was continued while the reaction cooled to ambient temperature, and then for a further 2 h.; the mixture was then filtered directly into an ethereal solution (20 cm³) of PCl₃ (4.5 cm³, 0.05 mol) held at −78 °C. The mixture was then stirred for 30 minutes at this temperature, before being allowed to warm to ambient temperature over the course of 18 h. The solution was filtered and the residues washed with Et₂O (3 x 15 cm³); the combined filtrate was stripped of Et₂O by distillation at ambient temperature to afford a colorless liquid (5.92 g, 67 %). ¹H NMR (CDCl₃): δ : 0.48 (s, 6H SiMe₂), 2.24 (d, ²J_{PH} = 15.2 Hz, CH₂), 2.37 (s, 3H, Me), 7.22 (d, ³J_{C-H} = 7.4 Hz, Ar-H), 7.44 (d, ³J_{C-H} = 7.4 Hz, Ar-H). ¹³C{¹H} NMR (CDCl₃): δ : −1.33 (s, SiMe₂), 21.6 (s, CH₃), 35.2 (d, ¹J_{C-P} = 61 Hz, CH₂), 129.1 (s, Ar-H), 133.1 (d, ³J_{C-P} = 4 Hz, Si-C), 133.7 (Ar-H), 140.0 (s, C-Me). ²⁹Si NMR (CDCl₃): −6.7. ³¹P NMR (CDCl₃): 203.3.

(*p*-Tol)Me₂SiC \equiv P. As previously described for RMe₂SiC \equiv P (R = Me, Ph),^{20,38} TolMe₂SiCH₂PCl₂ (0.595 g, 2.4 mmol) as solution in toluene was added to a toluene suspension of AgOTf (1.26 g, 4.9 mmol); after stirring 10 min., DABCO (0.550 g, 4.9 mmol) was added as solution toluene. After stirring for 1 h. the mixture was filtered and then calibrated for concentration by integration of its ³¹P{¹H}-NMR resonance (δ_p 103.3) against that of fully relaxed (*d*₁ = 150 s) PPh₃. Samples are stored below 5 °C (< 1 week) and recalibrated before use.

[Ru{P=CH(SiMe₂R)}Cl(CO)(PPh₃)₂] (R = Me 2, Ph 3, *p*-Tol 4). In a typical reaction, to a stirring suspension of [RuHCl(CO)(PPh₃)₂] (1.5 g, 1.53 mmol) in CH₂Cl₂ (15 cm³) was added an excess (1.3 equiv.) of RMe₂SiC \equiv P as solution in toluene (ca 25 cm³). After stirring for 1 h. the solvent was removed under reduced pressure to afford an orange/brown residue, which was washed vigorously with *n*-hexane (3 x 10 cm³). The solvent was then removed by filtration, to afford a

yellow to orange solid, which was dried in vacuo. **Data for 2:** Yield: 95 %. ¹H-NMR (C₆D₆, 499.9 MHz): δ_H 7.92 – 7.85 (m, 12 H, PAR₃), 7.39 (s, 1H, P=CH), 7.08 – 6.98 (m, 18 H, PAR₃), 0.18 (s, ¹J_{SiH} 6.5 Hz, 9 H). ¹³C{¹H}-NMR (C₆D₆) δ_C 203.0 (m, C \equiv O), 168.0 (br., CH, P=CH), 134.1, 132.2, 127.6 (m, CH, PAR₃ x 3), 0.9 (d, ¹J_{CP} 6.4 Hz, Si(CH₃)₃). ³¹P{¹H}-NMR (C₆D₆) δ_P 34.6 (d, ¹J_{PP} 8 Hz), 548.5 (t, ¹J_{PP} 8 Hz). ²⁹Si{¹H}-NMR (C₆D₆) δ_{Si} −9.4. ν_{CO} = 1920 cm^{−1}. Anal. Found: C, 60.91; H, 4.82; Calcd for C₄₁H₄₀ClO₃RuSi: C, 61.07; H, 5.00. X-ray quality crystals were obtained by storage of a saturated ether solution at 4 °C for several days. *Crystal data for 2:* C₄₁H₄₀ClO₃RuSi.C₄H₁₀O, *M*_w = 954.49, monoclinic, P2₁/c (no. 14), *a* = 9.7961(5), *b* = 34.2580(17), *c* = 14.8457(7) Å, β = 95.201(5)°, *V* = 4961.6(4) Å³, *Z* = 4, *D*_c = 1.278 Mg m^{−3}, μ (Cu-K α) = 4.491 mm^{−1}, *T* = 173(2) K, 9180 independent reflections, full-matrix *F*² refinement *R*₁ = 0.0876, *wR*₂ = 0.2864 on 6502 independent absorption corrected reflections [*I* > 2 σ (*I*); 2 θ_{max} = 141.8°], 473 parameters, CCDC 1036624

Data for 3: ¹H-NMR (CD₂Cl₂): δ_H 7.66 – 7.56 (m, 12 H, Ar₂), 7.50 – 7.41 (m, 8 H, Ar), 7.40 (s, 1H, P=CH), 7.39 – 7.29 (m, 12 H, Ar), 0.26 (s, ¹J_{SiH} 6.3 Hz, 6 H, SiMe₂). ¹³C{¹H}-NMR (CD₂Cl₂, 150.81 MHz, 298 K) δ_C 201.9 (t, ¹J_{PC} 15 Hz, C \equiv O), 163.7 (d, ¹J_{PC} = 77 Hz, CH, P=CH), 134.3 (t, ¹J_{PC} 5.5 Hz, CH, PAR), 133.5 (s, CH, Ph), 132.1 (t, ¹J_{PC} 23.2 Hz, C, PAR), 130.3 (s, CH, Ph), 128.5 (s, C, Ph), 128.2 (t, ¹J_{PC} 5.2 Hz, CH, PAR), 127.5 (s, CH, Ph), −1.3 (d, ¹J_{CP} 7.7 Hz, Si(CH₃)₂). ³¹P{¹H}-NMR (CD₂Cl₂) δ_P 553.8 (t, ¹J_{PP} 8 Hz), 33.7 (d, ¹J_{PP} 8 Hz). ²⁹Si{¹H}-NMR (C₆D₆) δ_{Si} −14.3. ν_{CO} = 1938 cm^{−1}. Anal. Found: C, 63.53; H, 4.75; Calcd for C₄₄H₄₂ClO₃RuSi: C, 63.63; H, 4.88. X-ray quality crystals were obtained by slow evaporation of a saturated CH₂Cl₂/hexane solution at ambient temperature. *Crystal data for 3:* C₄₄H₄₂ClO₃RuSi, *M*_w = 868.37, monoclinic, P2₁/c (no. 14), *a* = 19.6355(5), *b* = 11.9196(2), *c* = 19.5933(5) Å, β = 116.565(3)°, *V* = 4101.6(2) Å³, *Z* = 4, *D*_c = 1.406 Mg m^{−3}, μ (Cu-K α) = 5.346 mm^{−1}, *T* = 173(2) K, 7897 independent reflections, full-matrix *F*² refinement *R*₁ = 0.0267, *wR*₂ = 0.0714 on 7237 independent absorption corrected reflections [*I* > 2 σ (*I*); 2 θ_{max} = 143.6°], 479 parameters, CCDC 1036625

Data for 4: Yield: 59 %. ¹H-NMR (CD₂Cl₂, 499.9 MHz) δ_H 0.20 (s, 6H, Si(CH₃)₂), 2.31 (s, 3H, CH₃), 6.9–7.46, 7.55–7.61 (2 x m, 30H PAR₃, 4H C₆H₄, 1H P=C). ¹³C{¹H}-NMR (CD₂Cl₂) δ_C 1.4 (s, Si(CH₃)₂), 21.7 (s, Ar-CH₃), 127.3 (dd, J = 7 Hz, 9 Hz, P-Ar), 128.0 (t, J = 5 Hz), 128.8 (t, J = 5 Hz), 130.1 (*ipso*-CH) 129.8 (P-Ar), 129.5 (P-Ar), 130.9 (P-Ar), 132.8 (t, J = 23 Hz, PAR), 134.3 (*o*-CH), 135.0 (m, PAR), 135.7 (m, P-Ar), 136.5 (t, J = 23 Hz, P-Ar), 138.28 (*para*-CH), 165.2 (br., C=P), 202.5 (br, CO). ³¹P{¹H}-NMR (CD₂Cl₂) δ_P 33.7 (d, ¹J_{PP} 8 Hz, PPh₃), 552.6 (t, ¹J_{PP} 8 Hz, P=C). ²⁹Si{¹H}-NMR (CD₂Cl₂): δ_{Si} −14.4. ν_{CO} = 1936 cm^{−1}. Anal. Found: C, 64.02; H, 5.14; Calcd for C₄₇H₄₄ClO₃RuSi: C, 63.98; H, 5.03. X-ray quality crystals were obtained by slow evaporation of a saturated CH₂Cl₂ solution at ambient temperature. *Crystal data for 4:* C₄₇H₄₄ClO₃RuSi, *M*_w = 882.34, monoclinic, P2₁/c (no. 14), *a* = 19.6947(6), *b* = 12.0013(2), *c* = 19.7876(5) Å, β = 116.762(4)°, *V* = 4176.0(2) Å³, *Z* = 4, *D*_c = 1.403 Mg m^{−3}, μ (Cu-K α) = 5.259 mm^{−1}, *T* = 173(2) K, 6511 independent reflections, full-matrix *F*² refinement *R*₁ = 0.0384, *wR*₂ = 0.1118 on 5898 independent absorption corrected reflections [*I* > 2 σ (*I*); 2 θ_{max} = 123.6°], 490 parameters, CCDC 1036626.

[Ru(η¹-N-η²-P-C-P(pz)=CH(Bu))Cl(CO)(PPh₃)₂] (5). At ambient temperature, to a solution of pzH (0.010 g, 0.150 mmol) in THF (5 cm³) was added ^tBuLi (0.06 cm³, 2.5M, 0.150 mmol). The mixture was stirred for ca 10 min. then transferred *via* cannula to a stirred solution of **1** (0.119 g, 0.150 mmol). After stirring for 1 h. the solvent was removed under reduced pressure, then the product extracted into CH₂Cl₂ (5 cm³), filtered and taken to dryness *in vacuo*. Yield: 0.078 g, 63 %. ¹H NMR (CD₂Cl₂) δ_H : 7.36–7.10 (m, 30 H, P(C₆H₅)), 6.91 (d, ¹J_{HH} = 2.26 Hz, 1 H, Pz-H³), 5.58 (br, 1 H, Pz-H²), 5.54 (m, 1 H, Pz-H¹), 2.84 (m, 1 H, P-CH), 0.88 (s, 9 H, C(CH₃)₃). ¹³C{¹H} NMR (CD₂Cl₂) δ_C : 211.7 (m, C \equiv O), 140.9 (s, Pz-C³), 135.9 (s, Pz-C⁵), 138.8–128.2 (m, P(C₆H₅)), 105.2 (s, Pz-C⁴), 81.6 (ddd, ¹J_{CP} = 68.65, 36.36, 4.83 Hz), CH^t Bu), 37.7 (d, ¹J_{CP} = 14.83 Hz, C(CH₃)₃), 33.4 (m, C(CH₃)₃). ³¹P{¹H} NMR (CD₂Cl₂) δ_P : 44.2 (dd, ¹J_{PP} = 17.45, 8.10 Hz), 42.5 (dd, ¹J_{PP} = 47.14, 17.42

Hz), 38.8 (dd, $J_{PP} = 47.02, 8.17$ Hz, $P=C$). ν_{CO}/cm^{-1} 1906. Anal Found: C, 62.34 %; H, 5.42 %; N, 3.58 %. Calcd for $C_{45}H_{43}P_3N_2OSiRu \cdot 0.75CH_2Cl_2$: C, 62.05 %; H, 5.07 %; N, 3.16 %.⁴⁵

[Ru($\eta^1-N-\eta^2-P,C-P(pz^*)=CH(Bu)$)(CO)(PPh₃)₂] (6). Prepared as for **5**, commencing with pz^*H (0.155 g, 0.160 mmol), ⁿBuLi (0.07 cm³, 2.5 M, 0.160 mmol) and **1** (0.126 g, 0.160 mmol). Yield: 0.090 g, 66 %. ¹H NMR (CD₂Cl₂) δ_H : 7.39–7.13 (m, 30 H, P(C₆H₅)), 5.14 (s, 1 H, Pz^*-H^4), 2.90 (ddd, $J_{HP} = 5.70, 3.28, 2.38$ Hz, ($^1J_{CH} = 137$ Hz), 1 H, $P-CH$), 1.96 (s, 3 H, Pz^*-CH_3-5), 0.91 (s, 9 H, C(CH₃)₃), 0.43 (s, 3 H, Pz^*-CH_3-3). ¹³C{¹H} NMR (CD₂Cl₂) δ_C : 211.8 (m, C=O), 152.4 (s, Pz^*-C^3), 145.6 (d, $J_{CP} = 1.63$ Hz, Pz^*-C^5), 134.7–134.2 (m, P(C₆H₅)), 129.5–128.0 (m, P(C₆H₅)), 105.6 (s, Pz^*-C^4), 79.8 (ddd, $J_{CP} = 66.67, 36.99, 5.43$ Hz, CH⁺ Bu), 37.7 (d, $J_{CP} = 13.72$ Hz, C(CH₃)₃), 34.0 (dd, $J_{CP} = 9.47, 3.67$ Hz, C(CH₃)₃), 12.1 (s, Pz^*-CH_3-3), 9.6 (d, $J_{CP} = 5.26$ Hz, Pz^*-CH_3-5). ³¹P{¹H} NMR (CD₂Cl₂) δ_P : 45.5 (dd, $J_{PP} = 17.28, 8.64$ Hz), 41.4 (dd, $J_{PP} = 50.36, 16.98$ Hz), 14.7 (dd, $J_{PP} = 50.44, 8.56$ Hz, $P=C$). ν_{CO}/cm^{-1} 1906. MS [FAB]: m/z (%): 850 [M⁺], 751 [M – Pz*]⁺, 655 [M – Pz* – PC(H)⁺Bu]⁺. Anal Found: C, 62.27 %; H, 5.41 %; N, 3.26 %. Calcd for $C_{47}H_{47}N_2OP_3SiRu$: C, 66.43 %; H, 5.57 %; N, 3.30 %.

[Ru($\eta^1-N-\eta^2-P,C-P(pz)=CH(SiMe_3)$)(CO)(PPh₃)₂] (7). Prepared as for **5** from pzH (0.010 g, 0.150 mmol), ⁿBuLi (0.06 cm³, 0.150 mmol) and **2** (0.121 g, 0.150 mmol). Yield: 0.090 g, 72 %. ³¹P{¹H} NMR (CD₂Cl₂, 161.7 MHz) δ_P : 58.7 (d, $J_{PP} = 47.78$), 46.6 (d, $J_{PP} = 18$ Hz), 42.0 (dd, $J_{PP} = 47, 18$ Hz). ¹H-NMR (CD₂Cl₂) δ_H : 7.38 – 7.30, 7.27 – 7.17, 7.12 – 7.06 (3 x m, 30 H, PAr₃) 6.89 (br. 1H, $pz-H^3$), 5.48 (br. 1H, $pz-H^5$), 5.45 (br. 1 H, $pz-H^4$), 1.59 (br., 1 H, $P-CH$), 0.18 (s, 9 H, Si(CH₃)₃). ¹³C{¹H} NMR (CD₂Cl₂) δ_C : 211.2 (m, C=O), 141.3 ($pz-C^3$), 135.7 ($pz-C^4$), 138.2 (m, *ipso*-PAr₃), 134.3, 129.0, 128.3 (3 x CH, PAr₃), 105.0 ($pz-C^5$), 47.6 (ddd, $J_{CP} = 79, 31, 4$ Hz, $P-CH(SiMe_3)$), 1.6 (*dm*, $J_{CP} = 5$ Hz, Si(CH₃)₃). ²⁹Si{¹H}-NMR (CD₂Cl₂) δ_{Si} : –1.38. $\nu_{CO} = 1906$ cm^{–1}. Anal. Found: C, 62.95%; H, 5.15%; N, 3.30. Anal. Calcd. For $C_{44}H_{43}P_3N_2OSiRu$: C, 63.08%; H, 5.13%; N, 3.34.

[Ru($\eta^1-N-\eta^2-P,C-P(pz^*)=CH(SiMe_3)$)(CO)(PPh₃)₂] (8). Prepared as for **6** from pz^*H (0.013 g, 0.135 mmol), ⁿBuLi (0.05 cm³, 0.125 mmol) and **2** (0.105 g, 0.120 mmol). Yield: 0.080 g, 77 %. ¹³C{¹H} NMR (CD₂Cl₂, 100.5 MHz) δ_C : 210.4 (m, C=O), 152.9 (pz^*-C^3), 145.7 (d, $J_{CP} = 1.4$ Hz, pz^*-C^5), 138.7 (C, *ipso*-PAr₃), 135.7, 129.5, 128.2 (3 x CH, PAr₃), 105.5 (d, $J_{CP} = 2.7$ Hz, pz^*-C^4), 44.9 (ddd, $J_{CP} = 78, 32, 5$ Hz, $P-CH(SiMe_3)$), 12.2 (s, pz^*-CH_3-3), 9.7 (s, pz^*-CH_3-5) 2.2 (*dm*, $J_{CP} = 6$ Hz, Si(CH₃)₃). ³¹P{¹H} NMR (CD₂Cl₂) δ_P : 46.6 (d, $J_{PP} = 17$ Hz), 39.3 (dd, $J_{PP} = 50, 17$ Hz), 32.9 (d, $J_{PP} = 47$ Hz). ¹H-NMR (CD₂Cl₂) δ_H : 7.58 – 7.53, 7.38 – 7.23, 7.21 – 7.13 (3 x m, 30 H, PAr₃), 5.12 (br., 1 H, $pz-H^4$), 1.62 (br., 1 H, $P-CH$), –0.13 (s, 9 H, Si(CH₃)₃). ²⁹Si{¹H} NMR (CD₂Cl₂) δ_{Si} : 1.28. $\nu_{CO} = 1907$ cm^{–1}. Anal. Found: C, 63.35%; H, 5.44%; N, 3.32. Anal. Calcd. For $C_{46}H_{47}P_3N_2OSiRu$: C, 63.52%; H, 5.41%; N, 3.22.

[Ru($\eta^1-N-\eta^2-P,C-P(pz)=CH(SiMe_2Ph)$)(CO)(PPh₃)₂] (9). Prepared as for **5** from pzH (0.020 g, 0.299 mmol), ⁿBuLi (0.12 cm³, 0.300 mmol) and **3** (0.260 g, 0.299 mmol). Yield: 0.137 g, 51%. ¹H NMR (CD₂Cl₂) δ_H : 7.47–7.07 (m, 35 H, P(C₆H₅) + Ph), 5.46 (br, 1 H, $Pz-H^4$), 7.52 (d, $J_{HH} = 2.08$ Hz, 1 H, $Pz-CH^5$), 6.81 (d, $J_{HH} = 2.08$ Hz, 1 H, $Pz-CH^3$), 1.72 (m, ($^1J_{CH} = 149$ Hz), 1 H, CHSi), 0.13 (s, 3 H, Si(CH₃)₂), –0.08 (s, 3 H, Si(CH₃)₂). ¹³C{¹H} NMR (CD₂Cl₂) δ_C : 211.1 (br, C=O), 141.4 (s, $Pz-C^3$), 135.9 (s, $Pz-C^5$), 135.1–127.8 (m, P(C₆H₅)), 106.1 (br, $Pz-C^4$), 45.1 (ddd, $J_{CP} = 3.58, 29.40, 79.52$ Hz, CHSi), 0.3 (d, $J_{CP} = 4.33$ Hz, Si(CH₃)₂), –1.6 (d, $J_{CP} = 10.42$ Hz, Si(CH₃)₂). ³¹P{¹H} NMR (CD₂Cl₂) δ_P : 57.0 (d, $J_{PP} = 47.05$ Hz, $P=C$), 47.0 (d, $J_{PP} = 17.77$ Hz), 41.7 (dd, $J_{PP} = 46.98, 17.63$ Hz). ²⁹Si{¹H} NMR (CD₂Cl₂) δ_{Si} : –6.6. $\nu_{CO} = 1913$ cm^{–1}. Anal Found: C, 62.37%; H, 5.01%; N, 3.49%. Calcd for $C_{49}H_{45}N_2OP_3SiRu \cdot 0.5CH_2Cl_2$: C, 63.08 %; H, 4.92 %; N, 2.97 %.⁴⁵

[Ru($\eta^1-N-\eta^2-P,C-P(pz^*)=CH(SiMe_2Ph)$)(CO)(PPh₃)₂] (10). Prepared as for **6** from pz^*H (0.035 g, 0.368 mmol), ⁿBuLi (0.15 cm³, 0.375 mmol) and **3** (0.318 g, 0.367 mmol). Yield: 0.124 g, 37 %. ¹H NMR (CD₂Cl₂) δ_H : 7.50 (m, 5 H, Ar), 7.36–7.14 (m, 30 H, Ar) (PPh₃ + Ph), 5.12 (s, 1 H, Pz^*-H^4), 1.98 (br, 3 H, Pz^*-CH_3-5), 1.77 (br, 1 H, ($^1J_{CH} = 128.49$ Hz), CHSi), 0.43 (br, 3 H, Pz^*-CH_3-3), 0.17 (s, 3 H, Si(CH₃)), –0.02 (s, 3 H, Si(CH₃)). ¹³C{¹H} NMR (CD₂Cl₂) δ_C : 210.1 (m, C=O), 153.1

(s, Pz^*-C^3), 145.7 (d, $J_{CP} = 1.69$ Hz, Pz^*-C^5), 136.1–127.9 (m, P(C₆H₅)), 106.7 (d, $J_{CP} = 2.74$ Hz, Pz^*-C^4), 41.8 (ddd, $J_{CP} = 78.19, 32.40, 4.35$ Hz, CHSi), 12.1 (s, Pz^*-CH_3-3), 9.7 (d, $J_{CP} = 5.45$ Hz, Pz^*-CH_3-5), 0.5 (d, $J_{CP} = 8.78$ Hz, Si(CH₃)₂), –0.4 (d, $J_{CP} = 7.61$ Hz, Si(CH₃)₂). ³¹P{¹H} NMR (CD₂Cl₂) δ_P : 47.0 (d, $J_{PP} = 16.46$ Hz, 38.9 (dd, $J_{PP} = 50.75, 16.67$ Hz), 32.3 (d, $J_{PP} = 50.21$ Hz, $P=C$). ²⁹Si{¹H} NMR (CD₂Cl₂) δ_{Si} : –4.9. $\nu_{CO} = 1910$ cm^{–1}. Anal Found: C, 65.87 %; H, 5.29 %; N, 3.09 %. Calcd for $C_{51}H_{49}P_3N_2OSiRu$: C, 66.01 %; H, 5.32 %; N, 3.02 %.

[Ru($\eta^1-N-\eta^2-P,C-P(pz')=CH(SiMe_3)$)(CO)(PPh₃)₂] ($pz' = pz^{H,CF_3}$ 11; pz^{Me,CF_3} 12). Prepared in analogous fashion to **7** and **8**, by lithiation of the respective $pz'H$, and subsequent addition to **1** equiv. **2** as solution in thf. **Data for 11:** ¹H NMR (CDCl₃) δ_H : 7.39–7.16 (br. m, 24 H, C₆H₅), 7.07 (br. m, 6 H, C₆H₅), 5.59 (s, 1 H, $Pz^{CF_3}-H^4$), 5.28 (s, 1 H, $Pz^{CF_3}-H^3$) 1.78 (br. s, 1 H, CHSi), –0.17 (s, 9 H, Si(CH₃)₃). ¹³C{¹H} (CDCl₃) δ_C : 190.0 (C=O), 137.3 (m, C, PC₆H₅ *ipso*); 135.9 (s, $Pz^{CF_3}-C^5$), 133.6 (m, CH, PC₆H₅) 128.6 (obscured, q, $J_{CF} = 248$ Hz, CF₃), 127.9 (m CH, PC₆H₅), 0.98 (s, SiCH₃) remaining resonances not resolved. ³¹P{¹H} NMR (CDCl₃) δ_P : 76.6 (dq, $J_{PP} = 43.68$ Hz, $J_{PF} = 18.40$ Hz, $P=C$), 47.7 (d, $J_{PP} = 18.13$ Hz), 41.5 (dd, $J_{PP} = 43.85, 17.99$ Hz). ²⁹Si{¹H} NMR (CDCl₃) δ_{Si} : –1.1. ¹⁹F NMR (CDCl₃) δ_F : –60.1 (d, $J_{FP} = 18.07$ Hz). $\nu_{CO} = 1912$ cm^{–1}. Anal Found: C, 59.60%; H, 4.52%; N, 3.15%. Calcd for $C_{45}H_{42}P_3F_3N_2OSiRu$: C, 59.67%; H, 4.64%; N, 3.09%. **Data for 12:** ¹H NMR (CDCl₃) δ_H : 7.45–7.41 (br.m, 6 H, C₆H₅), 7.27–7.20 (br. m, 18 H, C₆H₅), 7.16–7.12 (br. m, 6 H, C₆H₅), 5.52 (s, 1 H, $Pz^{Me,CF_3}-H^4$), 1.76 (s ($^1J_{CH} = 129.3$ Hz), 1 H, CHSi), 0.55 (s, 3 H, CH₃), –0.13 (s, 9 H, Si(CH₃)₃). ¹³C{¹H} NMR (CDCl₃) δ_C : 209.2 (br. m, C=O), 152.5 (br. m, $Pz^{Me,CF_3}-C^3$), 137.8 (dd, $J = 30.98, 1.60$ Hz, $Pz^{Me,CF_3}-C^5$), 134.3–133.6 (m, C₆H₅), 129.2–128.6 (m, C₆H₅), 128.0–127.7 (m, C₆H₅), 119.2 (q, $J_{CF} = 268$ Hz, CF₃), 105.6 (br. m, $Pz^{Me,CF_3}-C^4$), 45.2 (ddd, $J_{CP} = 80.06, 31.84, 4.63$ Hz, SiCH), 11.8 (s, $Pz^{Me,CF_3}-CH_3-3$), 1.7 (dd, $J_{CP} = 5.83, 1.40$ Hz, Si(CH₃)₃). ³¹P{¹H} NMR (CDCl₃) δ_P : 64.6 (dq, $J_{PP} = 46.79$ Hz, $J_{PF} = 20.19$ Hz, $P=C$), 46.9 (dd, $J_{PP} = 16.85, 1.09$ Hz), 38.4 (ddq, $J_{PP} = 46.79, 16.86$ Hz, $J_{PF} = 1.79$ Hz). ²⁹Si{¹H} NMR (CDCl₃) δ_{Si} : 2.2. ¹⁹F NMR (CDCl₃) δ_F : –60.0 (d, $J_{FP} = 20.13$ Hz). $\nu_{CO} = 1909$ cm^{–1}. Anal. Found: C, 59.90%; H, 4.72%; N, 2.98. Anal. Calcd. For $C_{46}H_{44}F_3P_3N_2OSiRu$: C, 60.07%; H, 4.82%; N, 3.04.

[Ru($\eta^1-N-\eta^2-P,C-P(pz')=CH(SiMe_2Ph)$)(CO)(PPh₃)₂] ($pz' = pz^{H,CF_3}$ 13; pz^{Me,CF_3} 14). Prepared in analogous fashion to **7** and **8**, by lithiation of the respective $pz'H$, and subsequent addition 1 equiv. **2** as solution in thf. Compound **14** forms alongside decomposition products, limited purification being achieved by extraction into hexane.³⁴ This compound is characterized spectroscopically ‘*in situ*’. **Data for 13:** ¹H NMR (CDCl₃) δ_H : 7.61 (br.m, 2 H, Si(C₆H₅)), 7.41–7.18 (br. m, 27 H, C₆H₅), 7.08 (br.m, 6 H, C₆H₅), 5.61 (s, 1 H, $Pz^{CF_3}-H^4$), 5.36 (s, 1 H, $Pz^{CF_3}-H^3$), 1.97 (br.m, 1 H, CHSi), 0.18 (s, 3 H, Si(CH₃)), –0.03 (s, 3 H, Si(CH₃)). ¹³C{¹H} NMR (CDCl₃) δ_C : 198.1 (br.m, C=O), 142.3 (br.m, $Pz^{CF_3}-C^3$), 135.0–133.6 (m, C₆H₅), 129.9–127.3 (m, C₆H₅), 121.4 (q, $J_{CF} = 267$ Hz, CF₃), 103.3 (br.m, $Pz^{CF_3}-C^4$), 46.7 (m (br), SiCH), 0.15 (d ($J_{CP} = 5.24$ Hz), SiCH₃) remaining resonances are not resolved. ³¹P{¹H} NMR (CDCl₃) δ_P : 74.9 (dq, $J_{PP} = 44.45$ Hz, $J_{PF} = 17.60$ Hz, $P=C$), 48.0 (d, $J_{PP} = 17.68$ Hz), 41.3 (dd, $J_{PP} = 44.45, 17.68$ Hz). ²⁹Si{¹H} NMR (CDCl₃) δ_{Si} : –5.3. ¹⁹F NMR (CDCl₃) δ_F : –60.1 (d, $J_{FP} = 19.48$ Hz). $\nu_{CO} = 1909$ cm^{–1}. High-res ESI+MS: m/z 968.1426 [M]⁺ (Err=2.07 ppm). Anal. Found: C, 61.86%; H, 4.49%; N, 3.00. Anal. Calcd. For $C_{50}H_{44}F_3P_3N_2OSiRu$: C, 62.05%; H, 4.58%; N, 2.89. **Data for 14:** ¹H NMR (CDCl₃) δ_H : 7.42 (br. m, 12 H, C₆H₅), 7.23 (br. m, 14 H, C₆H₅), 7.15 (br. m, 9 H, C₆H₅) (PPh₃ + Ph), 5.53 (s, 1 H, $Pz^{Me,CF_3}-H^4$), 1.97 (br. s, 1 H, $^1J_{CH} = 134.52$ Hz, CHSi), 0.56 (s, 3 H, CH₃), 0.19 (s, 3 H, Si(CH₃)), 0.01 (s, 3 H, Si(CH₃)). ¹³C{¹H} NMR (CDCl₃) δ_C : 209.0 (br. m, C=O), 152.6 (br. m, $Pz^{Me,CF_3}-C^3$), 143.2 (br. m, *ipso*-C₆H₅), 134.3–133.6 (m, C₆H₅), 129.2–128.6 (m, C₆H₅), 128.0–127.5 (m, C₆H₅), 137.6 (dd, $J = 31.06, 1.36$ Hz, $Pz^{Me,CF_3}-C^5$), 119.4 (q, $J_{CF} = 270$ Hz, CF₃), 105.7 (br. m, $^1J_{CH} = 129.77$ Hz, $Pz^{Me,CF_3}-C^4$), 41.8 (ddd, $J_{CP} = 80.61, 31.43, 4.93$ Hz, SiCH), 11.9 (s, $Pz^{Me,CF_3}-CH_3-3$), 0.16 (d, $J_{CP} = 8.53$ Hz, SiCH₃), –1.2 (d, $J_{CP} = 7.66$ Hz, SiCH₃). ³¹P{¹H} NMR (CDCl₃) δ_P : 62.7 (dq, $J_{PP} = 47.06$ Hz, $J_{PF} = 19.69$ Hz, $P=CH$), 47.2 (d, $J_{PP} = 16.25$ Hz), 38.3 (dd, $J_{PP} = 47.03, 16.48$ Hz). ²⁹Si{¹H} NMR

(CDCl₃) δ_{Si} : -6.0. ¹⁹F NMR (CDCl₃) δ_{F} : -59.8 (d, ⁴J_{FP} = 19.48 Hz). ν_{CO} = 1915 cm⁻¹. High-res ESI+MS: *m/z* 982.1582 [M]⁺ (Err=4.57 ppm).

ASSOCIATED CONTENT

Supporting Information

Final atomic positions of optimized geometries for compounds **1** – **4**, **5** and **7** in xyz format; frontier orbital plots for **1** – **4**; charge distribution plots for **1** and **2** and crystallographic data for compounds **2** (CCDC 1036624), **3** (CCDC 1036625) and **4** (CCDC 1036626) in cif format. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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DEDICATION

Dedicated to the memory of Professor Michael F. Lappert; an inspiring colleague.

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